تفريغ فيزيكال

اسم الموضوع: Buffered solutions

إعداد الصيدلاني/ـة: ياسمين خليل

بسم الله الرحمن الرحيم

- اللهم إني اسألك توبة قبل الموت ، وشهادة عند الموت ومغفرة بعد الموت و أماناً عند لقاءك وذهبياً من الجنة لي ولوالديّ وللمسلمين والمسلمات أجمعين
- اللهم اهدني كما اختلف فيه من الحق بإذنك
- اللهم إني اسألك العافية في الدنيا والآخرة
- اللهم اغفر لي ولوالديّ وللمسلمين والمسلمات الأحياء والأموات
- اللهم ارزقني لذة طاعتك واحرمني لذة معصيتك
- اللهم أغنني بحلالك عن حرامك واغنني بفضلك عمن سواك ❤
- سبحان الله ، الحمد لله ، لا إله إلا الله ، الله أكبر ، استغفر الله وأتوب إليه ، لا حول ولا قوة إلا بالله
- اللهم انصر الاسلام والمسلمين واهزم أعداء الاسلام وأعوانهم فإنهم لا يعجزونك

وحسبنا الله ونعم الوكيل

Buffered solutions

المحلول المنظم = قاعدة ضعيفة + حمضها المرافق (ملح)
= حمض ضعيف + قاعدته المرافقة (ملح)

Introduction

- Buffers are mixtures of compounds that resists changes in pH upon the addition of small quantities of acid or alkali.
- A buffer is composed of a weak acid (HA) and its salt (conjugate base A^-) or a weak base (B) and its conjugate acid BH^+.

Buffers: substances used to minimized the change of concentration of H^+ or OH^-

• buffer resists change of PH when a small amount of strong acid or base is added

يقاوم تغير PH بحال ضفنا كمية صغيرة من قاعدة أو حمض قوية

for example :-
1 L Human blood + HCl 0.01 mol
PH: 7.4 + small amount = 7.3
نلاحظ انه قيمة PH ما تغيرت إلا شوي

for example:- [weak acid, it's salt]
acetic acid + Sodium acetate
CH_3COOH CH_3COONa

[weak base, it's salt]
ammonia + ammonium chloride
NH_3 + NH_4Cl

• water can't resist the change of PH

- Acidic Buffer : (pH<7) weak acid + it's salt
  Basic Buffer : (pH>7) weak base + "

- Strong acid has the ability to donate a protone more easily than weak base

- Strong base has the ability to accept a proton more easily than weak base

Buffer Equation

The pH of a buffer solution can be calculated by use of the *buffer equation.*

E.g. When sodium acetate ($NaAc$) is added to acetic acid (HAc), the salt and the acid have an ion in common

$HAc \leftrightarrow H_3O^+ + Ac^-$

$NaAc \rightarrow Na^+ + Ac^-$

K_a for the weak acid is momentarily disturbed because the Ac^- supplied by the salt increases the $[Ac^-]$ term in the numerator:

$$K_a = \frac{[H_3O^+][Ac^- \uparrow]}{[HAc]}$$

$$pH = pKa + \log \frac{[salt]}{[acid]}$$

$pH = -\log [H^+]$

Buffer Equation

To reestablish the constant K_a, $[H_3O^+]$ is instantaneously decreased, by shifting the equilibrium in the direction of the reactants (the ionization of acetic acid is repressed).

$HAc + H_2O \leftarrow H_3O^+ + Ac^-$

$$K_a = \frac{[H_3O^+ \downarrow][Ac^- \uparrow]}{[HAc]}$$

Since weak acid is slightly ionized, $[HAc]$= [total acid concentration]

Since the salt is completely ionized, $[Ac^-]$ = [total salt concentration]

$$K_a = \frac{[H_3O^+][Salt]}{[acid]}$$

By rearranging the equation and using the logarithmic form:

$$pH = pKa + \log \frac{[salt]}{[acid]}$$

$pH = -\log [H^+]$

Buffer Equation

The previous equation is known as the *buffer equation* or the *Henderson–Hasselbalch equation*.

For a weak acid (HA) and its salt (S):

$$pH = pKa + \log \frac{[S]}{[HA]}$$

$-\log Ka$ — $[S]$ → ملح — $[HA]$ → حمض ضعيف

For a weak Base (B) and its salt (S):

$$pH = pKa + \log \frac{[B]}{[S]}$$

$[B]$ → قلوي — $[S]$ → قاعدة مرافقة

Buffer Equation

Example

What is the pH of a buffer solution containing 0.1 M acetic acid and 0.1 M sodium acetate?

تركيز حمض — تركيز ملح

$pKa = 4.76$ ← من السؤال بتجيبه

$$pH = pKa + \log \frac{[\text{ملح}]}{[\text{حمض}]}$$

$$pH = 4.76 + \log \frac{[0.1]}{[0.1]} =$$

$$4.76 + 0 =$$

$4.76 \rightarrow pH < 7 \rightarrow$ acid

Buffer Equation

Example

Volume → 0.1 L

n

How much sodium acetate (mol) should be added to 100 mL of 0.1 mol/L acetic acid solution to prepare a buffer of pH 5.2?

حمض

$pH = pKa + \log \frac{[\text{ملح}]}{[\text{حمض}]}$

$5.2 = 4.76 + \log \frac{[X]}{0.1} \rightarrow \log \frac{[X]}{0.1} = 0.44$

اللوغاريتم يتم توزيع
بحالة القسمة وبينهم بكون سالب

$\log x - \log 0.1 = 0.44 \rightarrow \log[x] - -1 = 0.44$

$X = 2.75$ mol/L

n + V العلاقة اللي بجمع

$n = V * M$

$n = 2.75 * 0.1 = 0.275$ mol

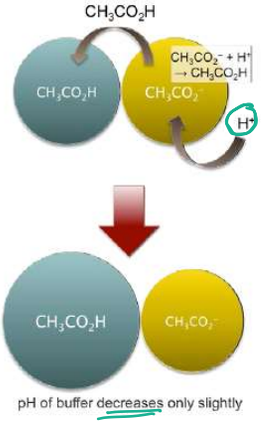
Buffer Capacity

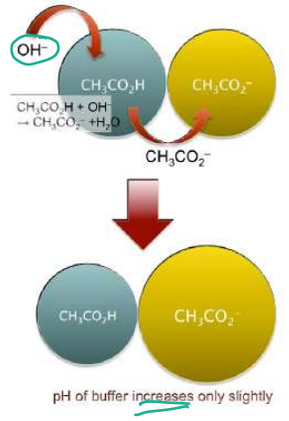
The amount of an acid/base that can be added to 1 L of buffer before significantly.

A weak acid and its conjugate base have buffering capacity because A^- ions remove the added H^+ as undissociated weak acid, while HA remove the added OH^- ions as water:

$A^- + H_3O^+ \rightarrow H_2O + HA$

$HA + OH^- \rightarrow H_2O + A^-$





Ion in common

H^+ + acid نوع معين

OH^- + acid عكس معين

Buffer Capacity

A weak base and its conjugate base have buffering capacity because B ions remove the added H^+ as undissociated weak acid, while BH^+ remove the added OH^- ions as water:

$$B + H_3O^+ \rightarrow H_2O + BH^+$$

$$BH^+ + OH^- \rightarrow H_2O + B$$

Buffer capacity is the quantity of strong acid or base that can be added to change the pH of one **liter** of buffer solution by one pH unit.

كمية الحمض القوي أو القاعدة القوية التي يمكن إضافتها قبل ما يبدأ الرقم الهيدروجيني pH بالتغير

كلما زادت BC كانت عندها القدرة على إضافة OH^-/H^+ أكثر قبل ما يبدأ pH بالتغير

Buffer Capacity

Koppel and Spiro and Van Slyke devised an approximate equation for calculating buffer capacity (β):

$$\beta = \frac{\Delta B}{\Delta pH}$$

ΔB → # of moles of strong base/acid

ΔB: number of moles of strong acid or base per liter of buffer.

ΔpH: change in pH.

When one of the buffer components is depleted completely, the solution lose its buffering capacity and can no longer resist the change in pH

نفذ

Buffer Capacity

Koppel and Spiro and Van Slyke developed a more exact Equation for calculating buffer capacity:

$$\beta = 2.3C\frac{K_a[H_3O^+]}{(K_a + [H_3O^+])^2}$$

C is the total buffer concentration (the sum of the molar concentrations of the acid and the salt).

This equation allows the calculation of buffer capacity at any pH (even when no acid or base has been added to the buffer).

The equation shows that an increase in the concentration of the buffer components (C) results in a greater buffer capacity (β).

C ↑ β ↑

Buffer Capacity

$[H^+] = ?$

At a hydrogen ion concentration of 1.75×10^{-5}, what is the capacity of a buffer containing 0.10 mole each of acetic acid and sodium acetate per liter of solution? ($Ka = 1.75 \times 10^{-5}$)

$[CH_3COOH] = 0.1$

$[CH_3COONa] = 0.1$

$C = [acid] + [salt] = 0.1 + 0.1 = 0.2$ mol

$$\beta = 2.3C\frac{K_a[H^+]}{(K_a + [H^+])^2}$$

$$= 2.3 \times 0.2 \times \frac{(1.75 \times 10^{-5})(1.75 \times 10^{-5})}{(1.75 \times 10^{-5} + 1.75 \times 10^{-5})^2}$$

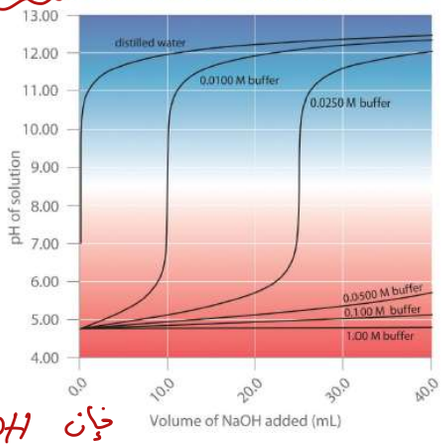
$$= 0.115 \text{ mol/L}$$

Buffer Capacity

The buffer capacity depends on:

(a) the value of the ratio [Salt]/[Acid], (buffer capacity increases as the ratio approaches 1)

(b) the magnitude of the individual concentrations of the buffer components (buffer capacity increases as the salt and acid concentrations are increased).



كل ما كانت تركيزات المكونات أعلى ← BC ← pH ← تزداد بس شوي بالتالي فإن تزداد أكثر، مثال:

Buffer 1

$[A^-] = 0.90\ M$
$[HA] = 0.49\ M$

التركيز هو أعلى صنا لحلول ← بالتالي تضيف pH بمعال إضافة قاعدة قوية ← يكون قليل ← وهذا يعني أعلى صنا لحلول ← BC

Buffer 2

$[A^-] = 0.090\ M$
$[HA] = 0.049\ M$

Buffer Capacity

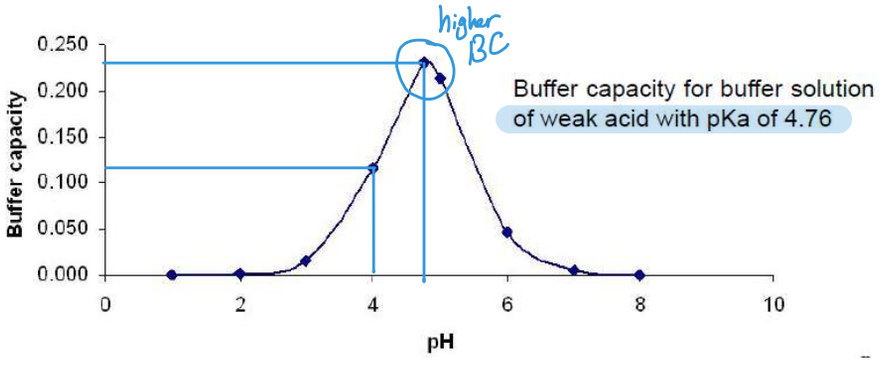
أعلى شي

The maximum buffer capacity occurs where $pH = pK_a$, or, in equivalent terms, where $[H3O+] = K_a$.

$$\beta_{max} = 0.576\,C$$

صفقاهدول نفس الشي

Where C is the total buffer concentration



$([H_3O^+] = Ka)^{-\log}$

$pH = pKa$

Buffer Capacity

Example

B_{max} ?

What is the maximum buffer capacity of an acetate buffer with a total concentration of 0.020 mole/liter?

$c = 0.02$

$B_{max} = 0.576\,C$

$= 0.576 \times 0.02$

$= 0.01152$ mol/L

basic

pH of tears = 7-8

basic

pH of blood = 7.4

Buffer in Biological Systems

Some body fluids have natural buffer capacity:

1. pH of tears (دموع) is 7-8 with higher buffer capacity so that a reasonably wide pH range of medicines can be tolerated.
2. pH of blood is maintained at approximately 7.4 by buffer component in the plasma (H_2CO) (bicarbonate and phosphate buffers) and erythrocytes (hemoglobin (Hb) and phosphate buffers).

$H_2CO_3 \leftrightarrow HCO_3^- + H^+$

$H_2PO_4 \leftrightarrow HPO_4^{2-} + H^+$

ion in Common

$HbH^+ + O_2 \leftrightarrow + O_2Hb + H^+$

Hb: hemoglobin, O_2Hb: oxyhemoglobin

هيموغلوبين حامل مرتبط أكسجين

Pharmaceutical Buffers

Buffer solutions are widely used to adjust pH of aqueous pharmaceutical solutions to ensure:

- Prevention of tissue irritation
- Optimum therapeutic effect
- Maximum drug stability
- Maximum drug solubility

Pharmaceutical Buffers

Tissue Irritation Prevention

- Solutions to be applied to delicate tissues (e.g. eye) or administered parenterally are liable to cause irritation if their pH is greatly different from the normal pH of the relevant body fluid.
- If there is a large pH difference between the solution and body fluid, tissue irritation will be minimal if:
  - The volume and buffer capacity of the solution is low
  - The volume and buffer capacity of the physiologic fluid is high.

Pharmaceutical Buffers

Maximum Therapeutic Effect vs Stability

- The undissociated form of a weakly acidic or basic drug often has a higher therapeutic activity than that of the dissociated salt form because they can penetrate body membranes readily due to their lipid solubility.
- The pH for maximum stability of a drug for ophthalmic use may be far below that of the optimum physiologic effect.
- Under such conditions, the solution of the drug can be buffered at a low buffer capacity and at a pH that is between that of optimum stability and that for maximum therapeutic action.
- When the solution is instilled in the eye, the tears bring the pH to about 7.4, converting the drug to the physiologically active form

Cause tear's pH is 7-8

Pharmaceutical Buffers

Maximum Solubility

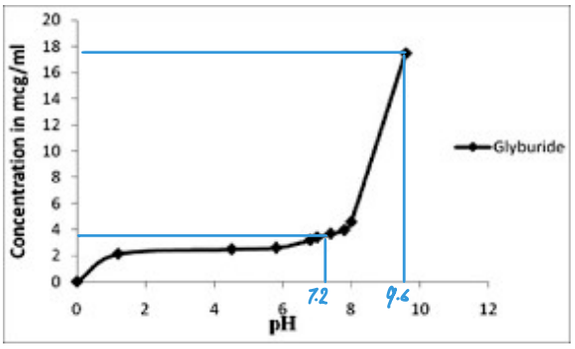
- The pH of the solution can affect the solubility of the drug.
- At a low pH, a base is predominantly in the ionic form, which is usually very soluble in aqueous media.
- As the pH is raised, more undissociated base is formed, which has poor water solubility, leading to precipitation of this form from solution.
- Therefore, the solution should be buffered at a sufficiently low pH so that the concentration of the free base is less than its solubility.

So become more soluble in an aqueous media

Pharmaceutical Buffers

pH Solubility profile

high pH → more solubility



Pharmaceutical Buffers

- **pH Stability profile**